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Interfacial Layer Effects in $Ba_{1-x}Sr_xTiO_3$ Thick Films prepared by Plasma Spray

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ABSTRACT

The dielectric properties of high k dielectric thick films prepared by thermal spray were investigated. $BaTiO_3$ and $Ba_{0.68}Sr_{0.32}TiO_3$ thick films were deposited using plasma spray on Ag·Pd screen-printed alumina substrates. The sprayed films were predominantly polycrystalline but contained an amorphous second phase. The dielectric constants of the films decreased with decreasing film thickness in 10 ~ 60 μm range. This was attributed to the presence of an interfacial layer between the film and the substrate as determined by capacitance measurements. The capacitance density of the interfacial layer was determined to be ~ 2.7 nF/cm^2. The capacitance density of the interfacial layer increased to 12 nF/cm^2 after post heat treatment at 500 °C for 20 hours.

INTRODUCTION

Direct writing of passive components including capacitors, resistors, and inductors is being actively considered to simplify the fabrication process and provide greater flexibility compared to conventional processes such as tape casting, screen printing, and lamination [1,2]. Thermal spray is under development as one possible approach. Thermal spray is a continuous and directed spray process in which melted particles are accelerated to high velocities and impinge on a substrate, where thin splats are formed by rapid solidification. The successive impingement of the molten particles results in the formation of thick films.

Various electronic materials have been deposited using thermal spray for electronic applications including conductors, resistors, insulators, inductors, capacitors, and sensors [3,4]. Structural and dielectric properties of thermal spray deposited high k dielectrics such as $BaTiO_3$ and $Ba_{0.68}Sr_{0.32}TiO_3$ were investigated for capacitor applications [5,6]. The dielectric constant of the as-deposited films was lower than the bulk ceramics. The reduced dielectric constants in thermal spray deposited high k dielectric films have been attributed to the presence of an amorphous phase, porosity, and fine grain size.

In this study, the dielectric properties of the high k dielectric films were investigated as a function of film thickness. The presence of a low dielectric constant interfacial layer between the film and the substrate was shown from the thickness dependence of the dielectric constants. The effect of the interfacial layer on the dielectric constant was examined using a series capacitance model. The thermal stability of the interfacial layer was determined by post heat treatment.

Table 1. Sample list used in this study.

Sample	Composition	Thickness (μm)
BT1	$BaTiO_3$	60
BT2	$BaTiO_3$	50
BST	$Ba_{0.68}Sr_{0.32}TiO_3$	40

EXPERIMENTAL DETAILS

$BaTiO_3$ and $Ba_{0.68}Sr_{0.32}TiO_3$ (BST) powders used in this study were purchased from Trans Tech Inc and the feed powder size was -325 mesh (<44 μm). $BaTiO_3$ and BST thick films were deposited using a Plasma Technik F4 plasma spray torch onto Ag·Pd (70/30) screen-printed alumina substrates. The thick films used in this study are listed in Table I. Phase purity and crystallinity were determined by θ - 2θ X-ray diffraction scans with a Scintag four circle diffractometer (XDS 2000) using Cu Kα radiation.

To measure the dielectric properties, silver top electrodes were applied on the films, forming parallel plate capacitor structures. The screen-printed Ag·Pd layer on Al_2O_3 substrate was used as the bottom electrode. A schematic of the capacitor structure is shown in Figure 1. The dielectric properties were measured with an HP 4192A impedance analyzer. The thickness dependence of the dielectric constant was examined using a successive polishing method. The film thickness at each polishing step was measured with a micrometer and a Tencor P-10 profilometer.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the $BaTiO_3$ and BST thick films are shown in Figure 2. The as-deposited films contained an amorphous phase, evidenced by a highly diffuse peak in the range of 22 ~ 34 °. The amorphous phase in thermal spray deposited films is believed to be formed by rapid thermal quenching of sprayed molten powders during deposition. Besides the amorphous phase, no other secondary phases were observed. After post heat treatment at 500 °C for 20 hours in air, the amorphous peak disappeared, indicating crystallization of the amorphous phase during the heat treatment.

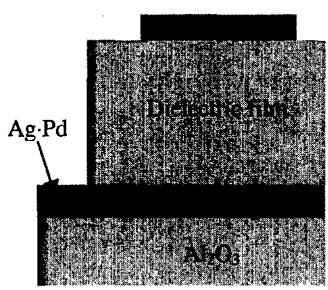

Figure 1. Schematic of the capacitor structure.

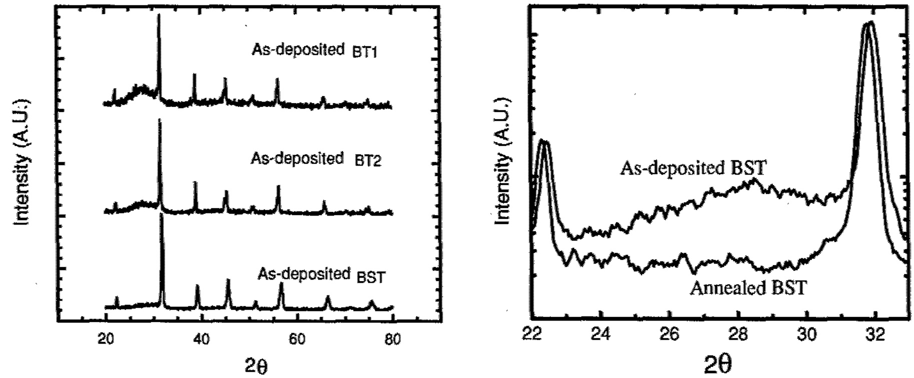

Figure 2. X-ray diffraction patterns of the as-deposited and annealed films.

The dielectric constant of the film was measured as a function of the film thickness and the results are shown in Figure 3. The dielectric constant decreased with the reduction of the film thickness for all samples. X-ray diffraction patterns obtained at various thicknesses showed that the crystallinity did not change with the film thickness. This suggests that the decrease in dielectric constants results from the presence of a low dielectric constant interfacial layer between the film and the substrate. In this case, the film and the interfacial layer are in series and the overall dielectric constant is affected by the low dielectric constant layer. The total capacitance density of the film can be expressed using a series capacitance model [7];

$$\frac{A}{C_{tot}} = \frac{A}{C_i} + \frac{A}{C_B} = \frac{t_i}{\varepsilon_i \varepsilon_0} + \frac{(t - t_i)}{\varepsilon_B \varepsilon_0} \tag{1}$$

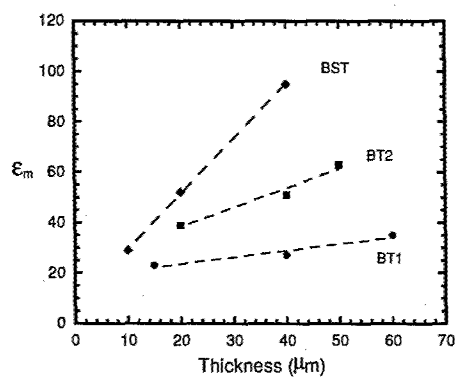

Figure 3. Dielectric constants at various thicknesses.

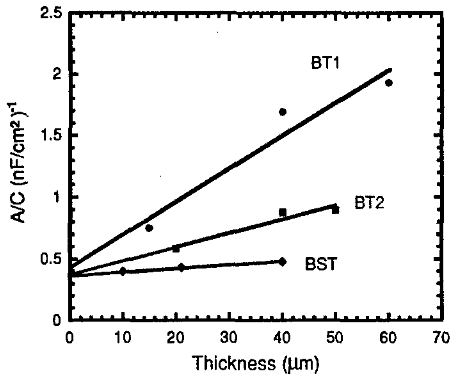

Figure 4. $(C/A)^{-1}$ vs. film thickness in as-deposited films.

where A is the area, C_{tot} is the total capacitance, C_B is the bulk film capacitance, C_i is the capacitance of the interfacial layer, ε_i is the permittivity of the interfacial layer, ε_0 is the permittivity of vacuum, ε_B is the permittivity of the bulk film, t_i is the interfacial layer thickness, and t is the total film thickness.

To investigate the effect of the interfacial layer on the dielectric constant of the film, the inverse of the capacitance densities, $(C/A)^{-1}$, was plotted as a function of the film thickness in Figure 4. In all samples, non-zero intercepts were obtained. The positive non-zero intercepts indicate the existence of a low dielectric constant interfacial layer. Using equation (1), when t is much larger than t_i, the capacitance density of the interfacial layer and the dielectric constant of the bulk film can be obtained from the intercept on the $(C/A)^{-1}$ axis and the slope of the plot, respectively.

From Figure 4, the bulk dielectric constant and the capacitance density of the interfacial layer were calculated. The results are presented with the measured dielectric constants in Table II. Differences in the bulk dielectric constants of the films are believed to be attributed to differences in the crystallinity of the films, as shown in Figure 2. In all films, the measured dielectric constant, ε_m, was lower than the bulk dielectric constant, ε_B, due to the presence of the low dielectric constant interfacial layer. The capacitance densities of interfacial layers were comparable in all samples, showing the interfacial layer thicknesses are similar in magnitude.

Table 2. Bulk dielectric constants and capacitance densities of the interfacial layer calculated from Figure 4, and the measured dielectric constants, ε_m.

Sample	ε_B	C_i/A (nF/cm^2)	ε_m
BT1	42	2.3	35
BT2	100	2.6	63
BST	420	2.7	95

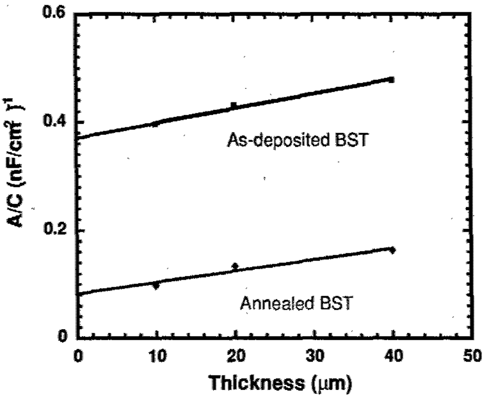

Figure 5. Inverse of capacitance density $(C/A)^{-1}$ vs. film thickness in as-deposited and annealed BST.

To determine the thermal stability of the interfacial layer, BST films were annealed at 500 °C for 20 hours in air. Dielectric properties of the annealed film were measured as a function of the thickness with the polishing procedure described above. The inverse of the capacitance densities of the as-deposited and annealed BST films are shown as a function of the film thickness in Figure 5. The bulk dielectric constant and the capacitance density of the interfacial layer were obtained using equation (1) and the results are presented in Table III. Note that the capacitance density of the interfacial layer, C_i/A, increased by one order of magnitude after annealing. From this, it is believed that the interfacial layer is an amorphous layer [8]. The increase in C_i/A implies the dielectric constant of interfacial layer increases presumably due to crystallization of the interfacial layer.

The bulk dielectric constant also increased after annealing, which was attributed to crystallization of the amorphous phase within the bulk film, as shown in Figure 2. It should be noted that the difference between ε_m and ε_B was significant for the as-deposited film. Moreover, the increase in ε_m is much larger than that in ε_B after annealing. This implies the measured dielectric constant is strongly influenced by the dielectric properties of the interfacial layer and the increase in the dielectric constant for the annealed film is mainly attributed to property changes in the interfacial layer.

Table 3. Bulk dielectric constants and capacitance densities of the interfacial layer calculated from Figure 5, and the measured dielectric constants.

Sample	ε_B	C_i/A (nF/cm^2)	ε_m
As-deposited BST	420	2.7	95
Annealed BST	540	12	280

CONCLUSIONS

$BaTiO_3$ and $Ba_{0.68}Sr_{0.32}TiO_3$ dielectric thick films were prepared by plasma spray. Dielectric properties of the films were investigated as a function of film thickness over the range of 10 ~ 60 μm. The dielectric constant decreased with decreasing film thickness, which was attributed to the presence of a low dielectric constant interfacial layer between the film and the substrate. The capacitance density of the interfacial layer in the as-deposited films was ~ 2.7 nF/cm^2, as determined using a series capacitance model. The interfacial layer was affected by post heat treatment at 500 °C and the capacitance density of the interfacial layer increased to 12 nF/cm^2 after the heat treatment. The increase of the dielectric constant in the annealed film is mainly attributed to changes in the capacitance density of the interfacial layer.

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